IMPLICATIONS OF METHANOL CROSSOVER IN DIRECT METHANOL FUEL CELLS

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DOE/ONR Fuel Cell Workshop

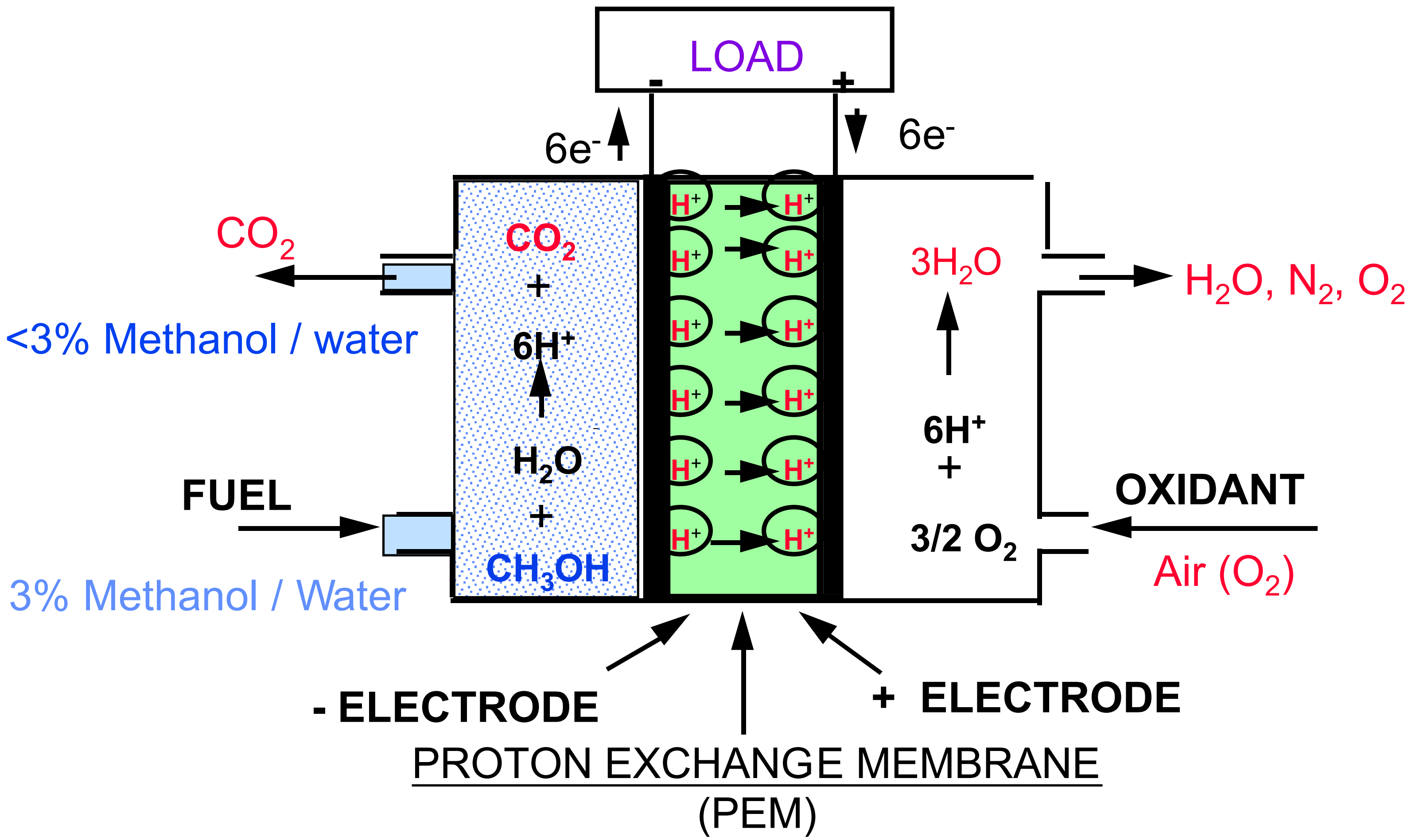
Baltimore, MD

Oct 6-8 1999

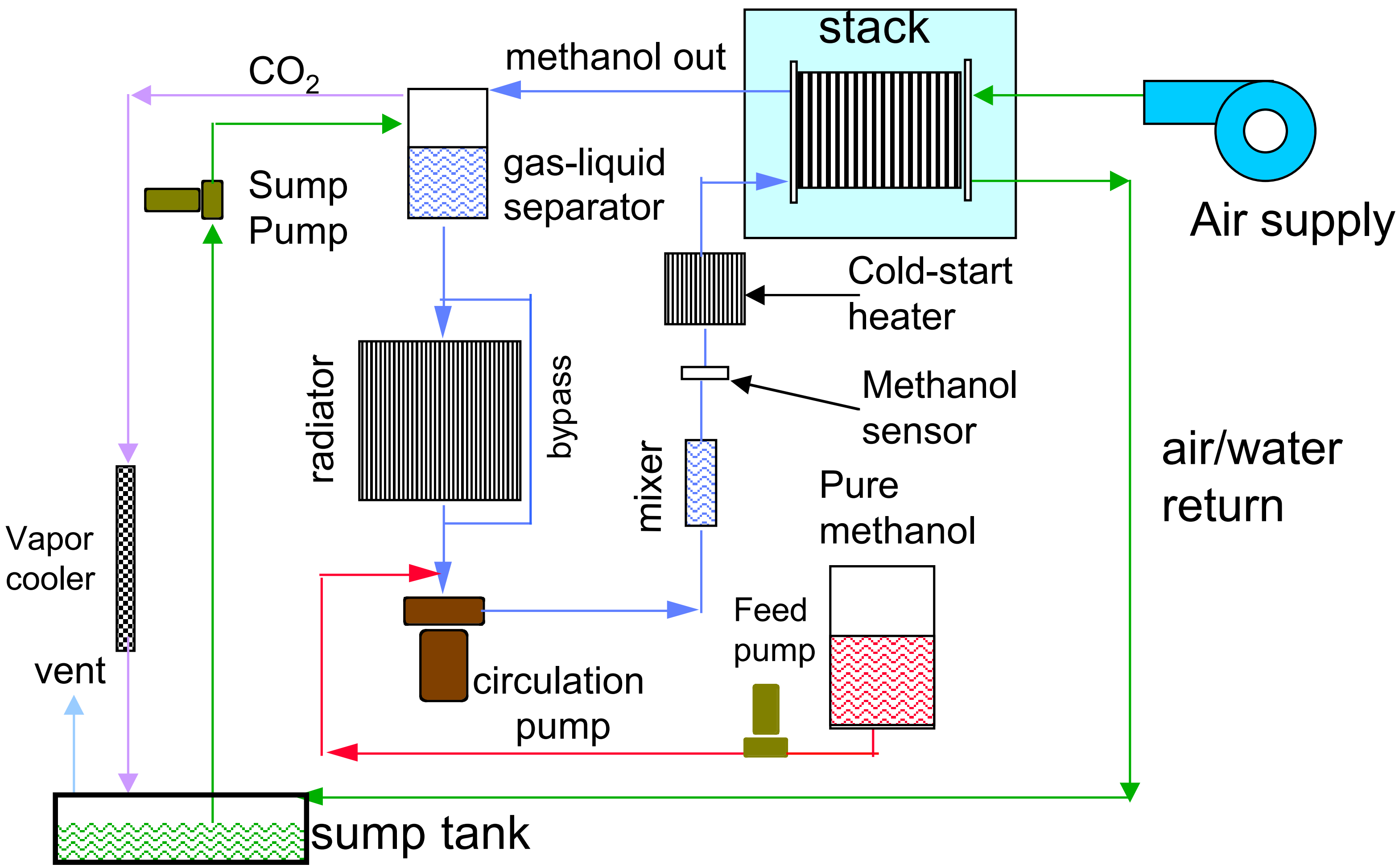
TEAM

- JPL
- University of Southern California
- Giner Inc
- Carnegie-Mellon university

DIRECT METHANOL LIQUID-FEED FUEL CELL



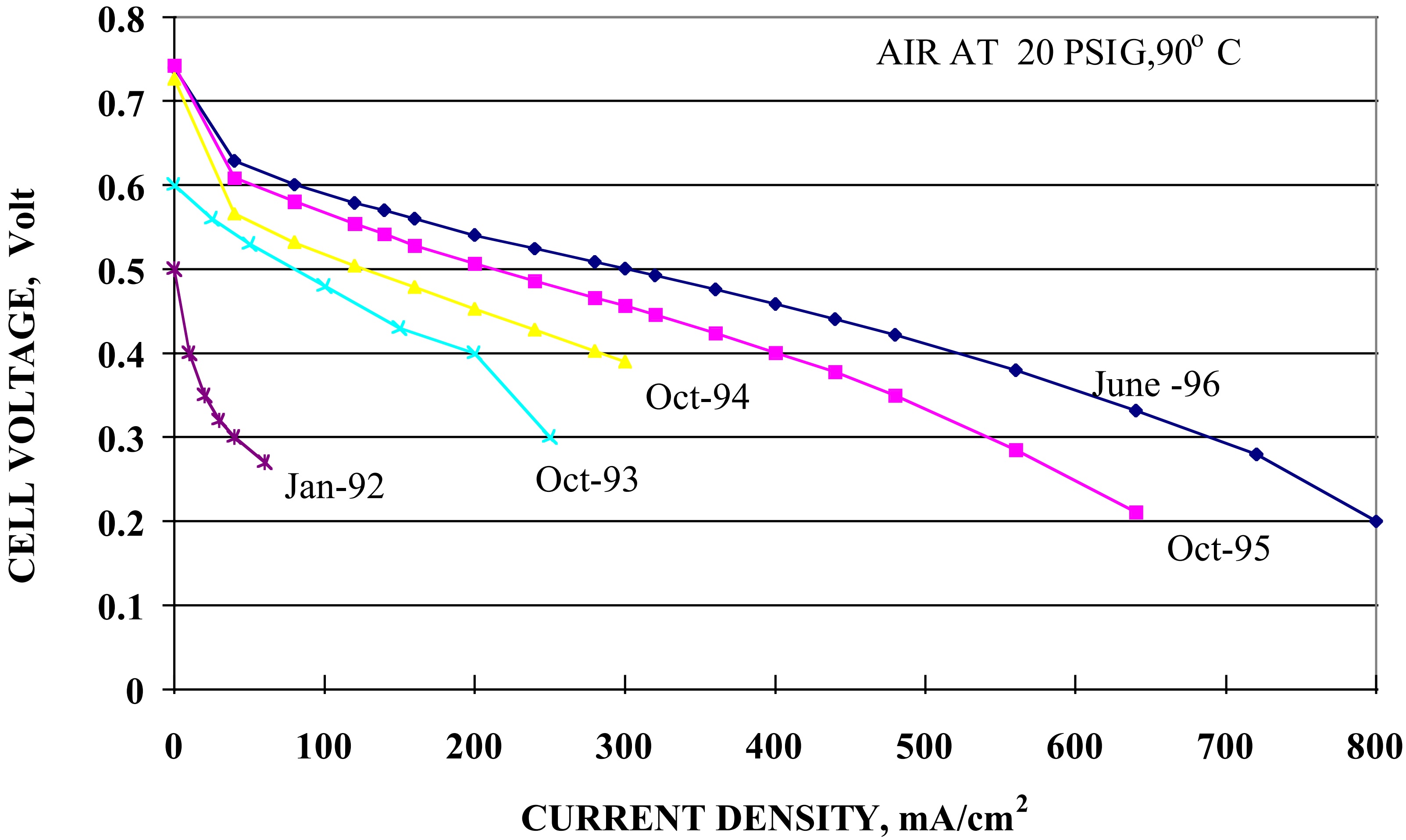
LAYOUT OF DIRECT METHANOL FUEL CELL SYSTEM



ADVANTAGES OF THE DIRECT METHANOL FUEL CELL SYSTEM

- SIMPLER THAN A REFORMER SYSTEM
- GOOD THERMAL CONTROL OF STACK
- SIMPLER STACK DESIGNS
- LOWER TEMPERATURE OF OPERATION COMPARED TO A REFORMER
- CAPABLE OF AMBIENT TEMPERATURE START-UP

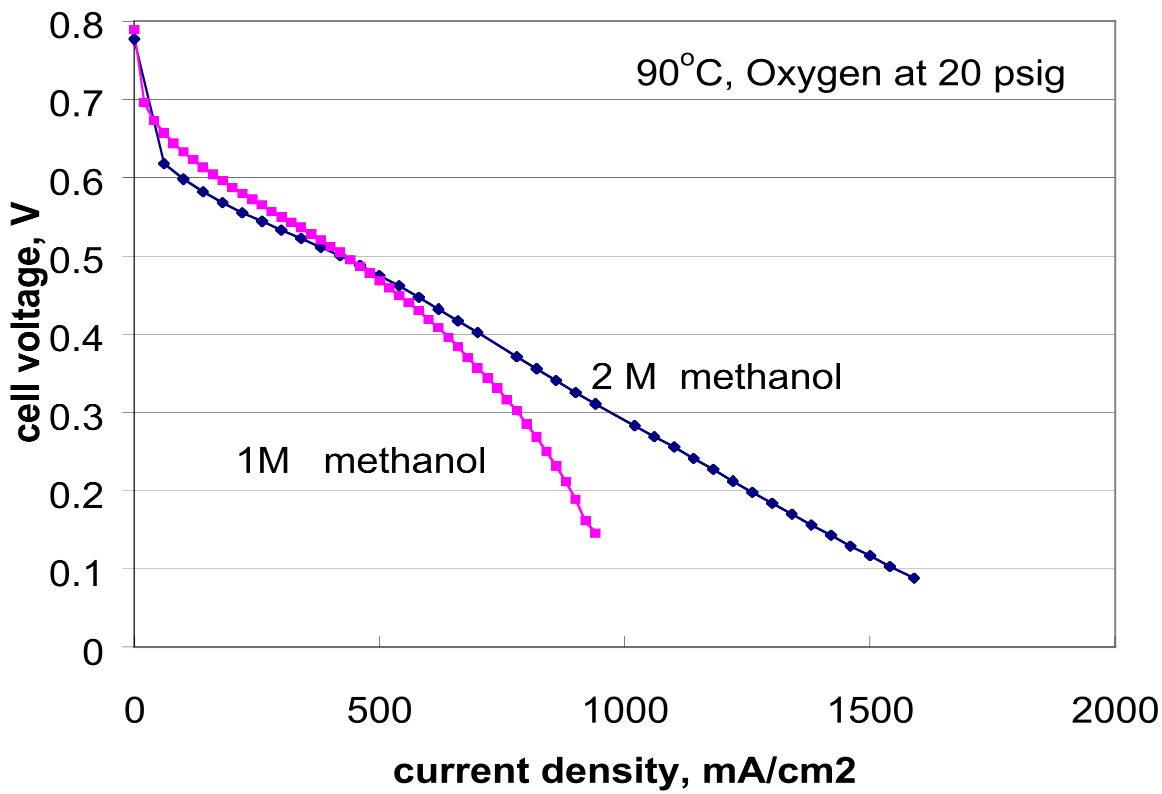
RECENT ADVANCES IN DIRECT METHANOL-AIR FUEL CELLS



TECHNICAL APPROACHES TO ADVANCES

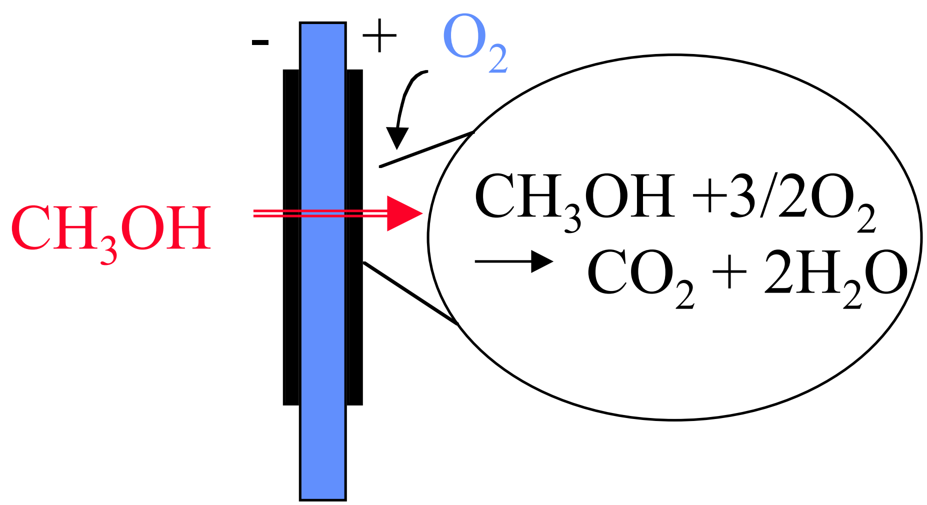
- Preparation of anode catalysts with high activity
- Improved methods of fabrication of membrane-electrode assemblies; improved catalyst utilization
- Modification to electrode structures to improve mass transfer
- Lowering fuel loss due to crossover :
  - new membranes, and modified electrode structures
- Fabrication of stacks and studying their electrical performance
- Obtaining system related information from experiments on stacks
- System modeling and integration studies

HIGH CURRENT DENSITIES WITH HIGH METHANOL CONCENTRATION



High concentrations allow attainment of high power densities
However, crossover of methanol is an issue at high concentrations

METHANOL CROSSOVER AND ITS IMPLICATIONS



Implications:

Parasitic fuel loss;20%

Lower cell voltage; by 0.1V

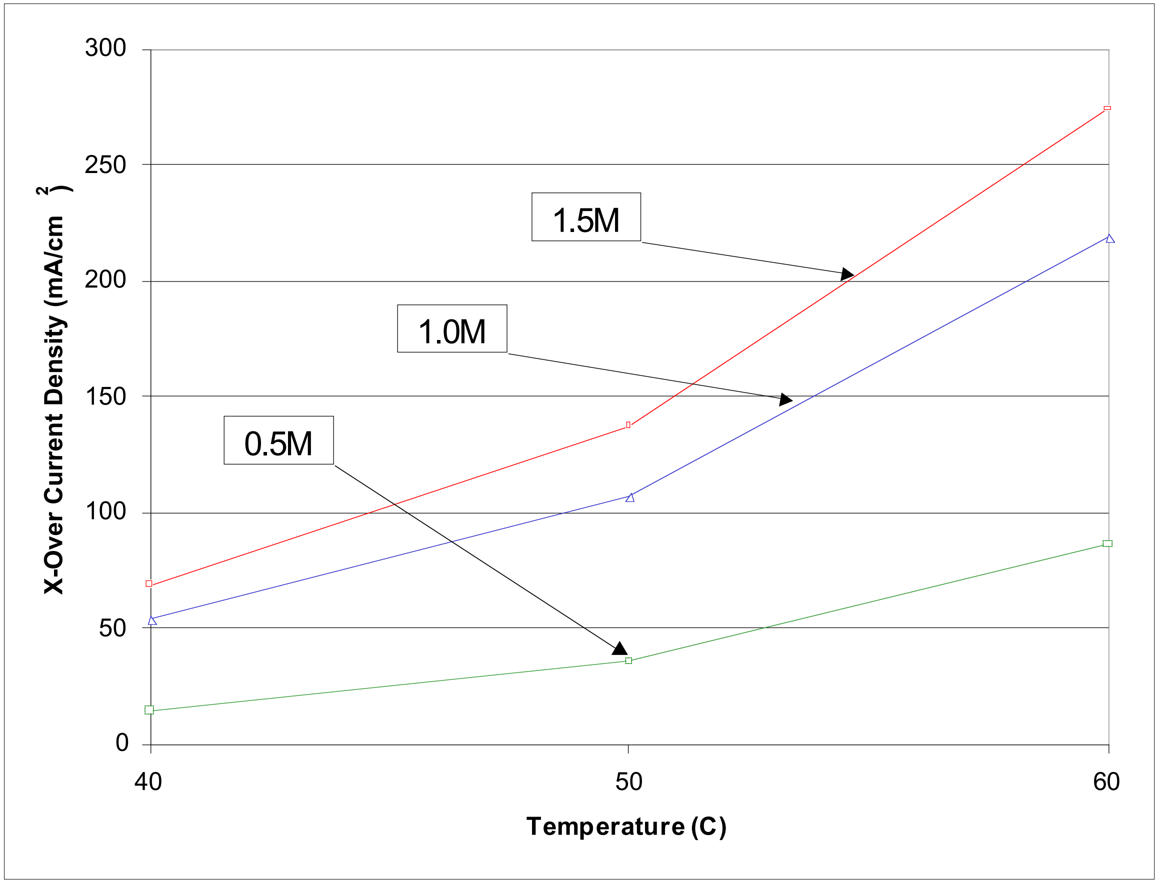
Increased air demand

Reduction in efficiency

MEASUREMENT OF CROSSOVER RATE

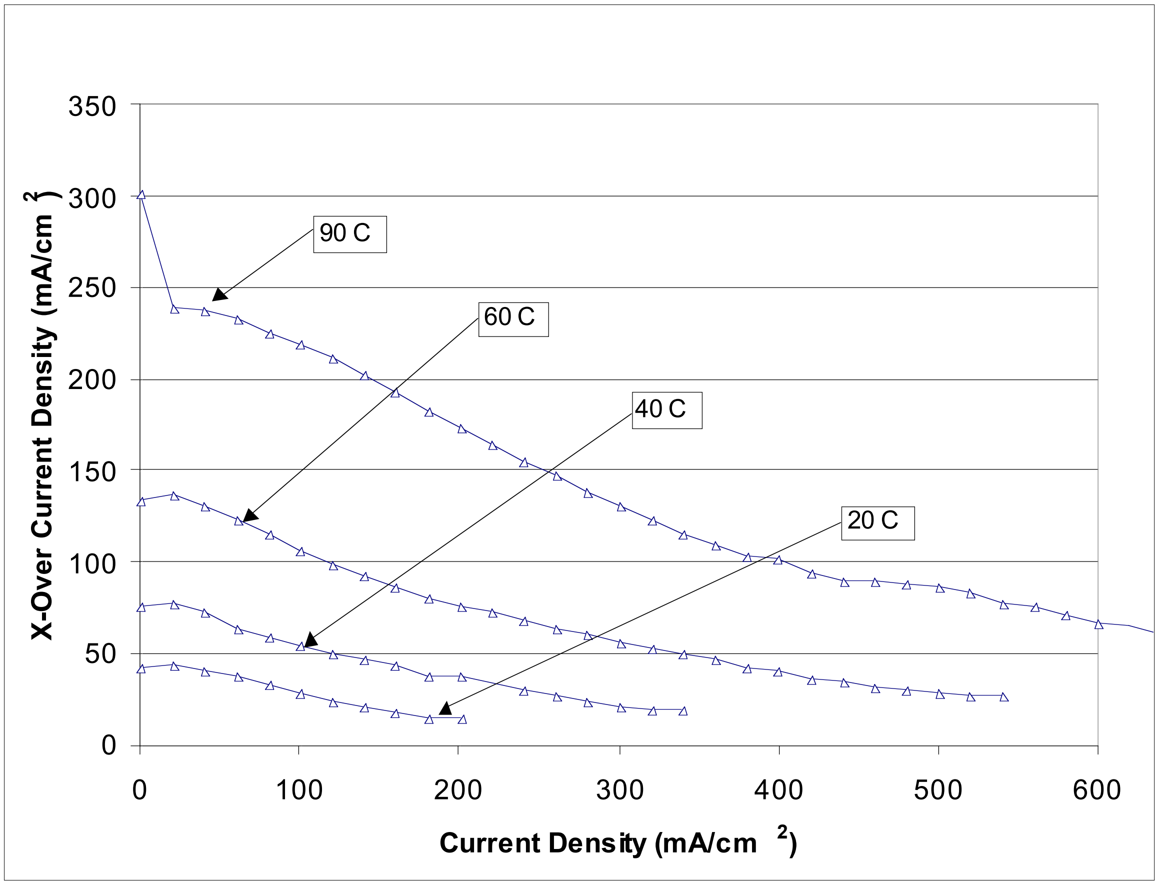
- CO_2 content of cathode stream (JPL)
  - in situ, electrode effects, effect of current density
- Estimation of limiting currents for transport of methanol through membrane
  - in-situ , electrode effects, effect of current density
- Permeation rate measurements through membranes
  - ex situ, only membrane properties
- Fuel Efficiency: (Coulombs $_{out}$)/ (Coulombs $_{In}$)
  - Most direct method, suited especially for large cells and large stacks.

CROSSOVER TEST
Open Circuit Measurements



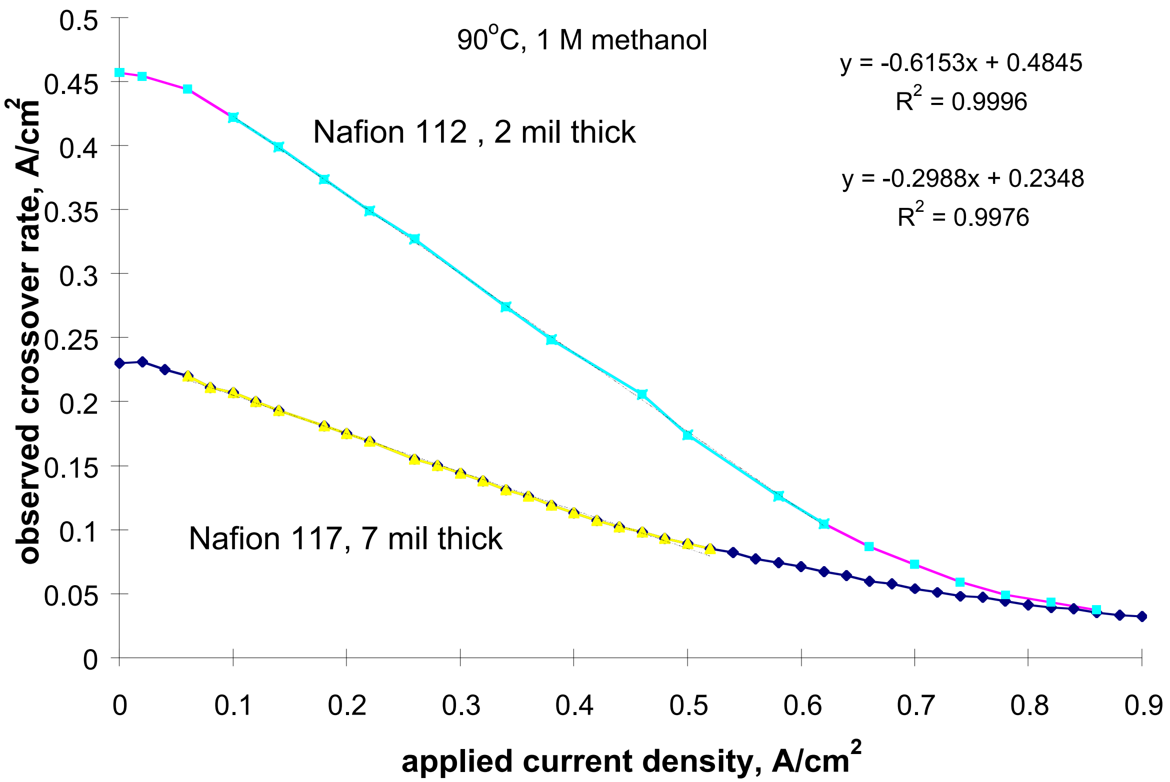
• **Crossover Current Density Increases With Temperature and Methanol Molarity.**

CROSSOVER RATE AND APPLIED LOAD AT 1.0 M METHANOL



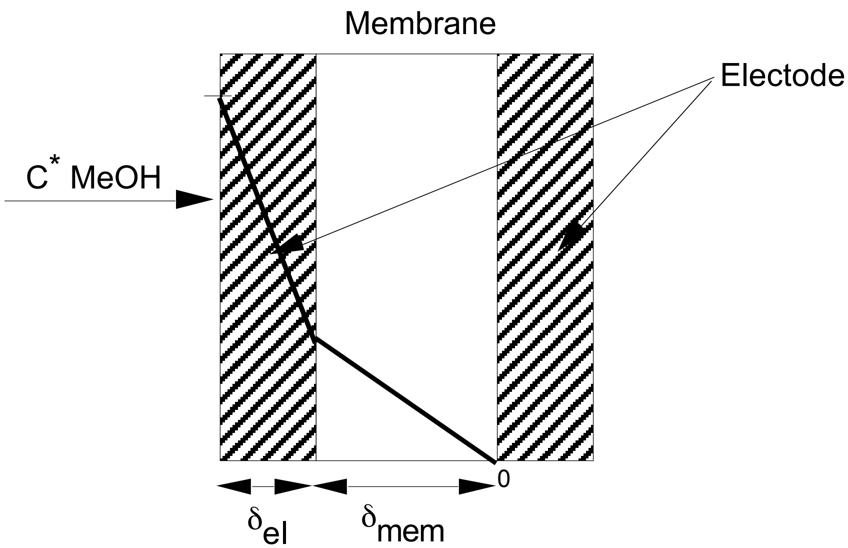
- **Crossover Current Density Decreases With Applied Current Density.**

DEPENDENCE OF CROSSOVER RATE ON APPLIED CURRENT DENSITY



Three separate regions seen in this dependence. The curve is dominated by a linear region and an asymptotic region.

ANALYSIS OF CROSSOVER RATE AND ITS DEPENDENCE ON APPLIED CURRENT DENSITY



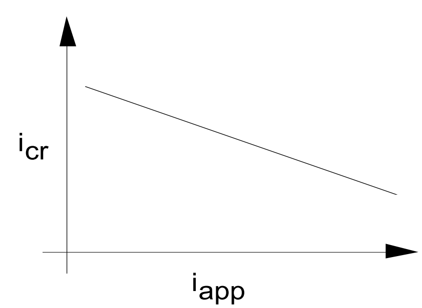
$$i_{cr} = nFAD_{el}\ \{ 1/(1+k)\}C^{*}/\delta_{el}\ \ -\ \ i_{app}\ \{1/(1+k)\}$$

where $k = D_{el}\,\delta_{mem}/(D_{mem}\,\delta_{el})$

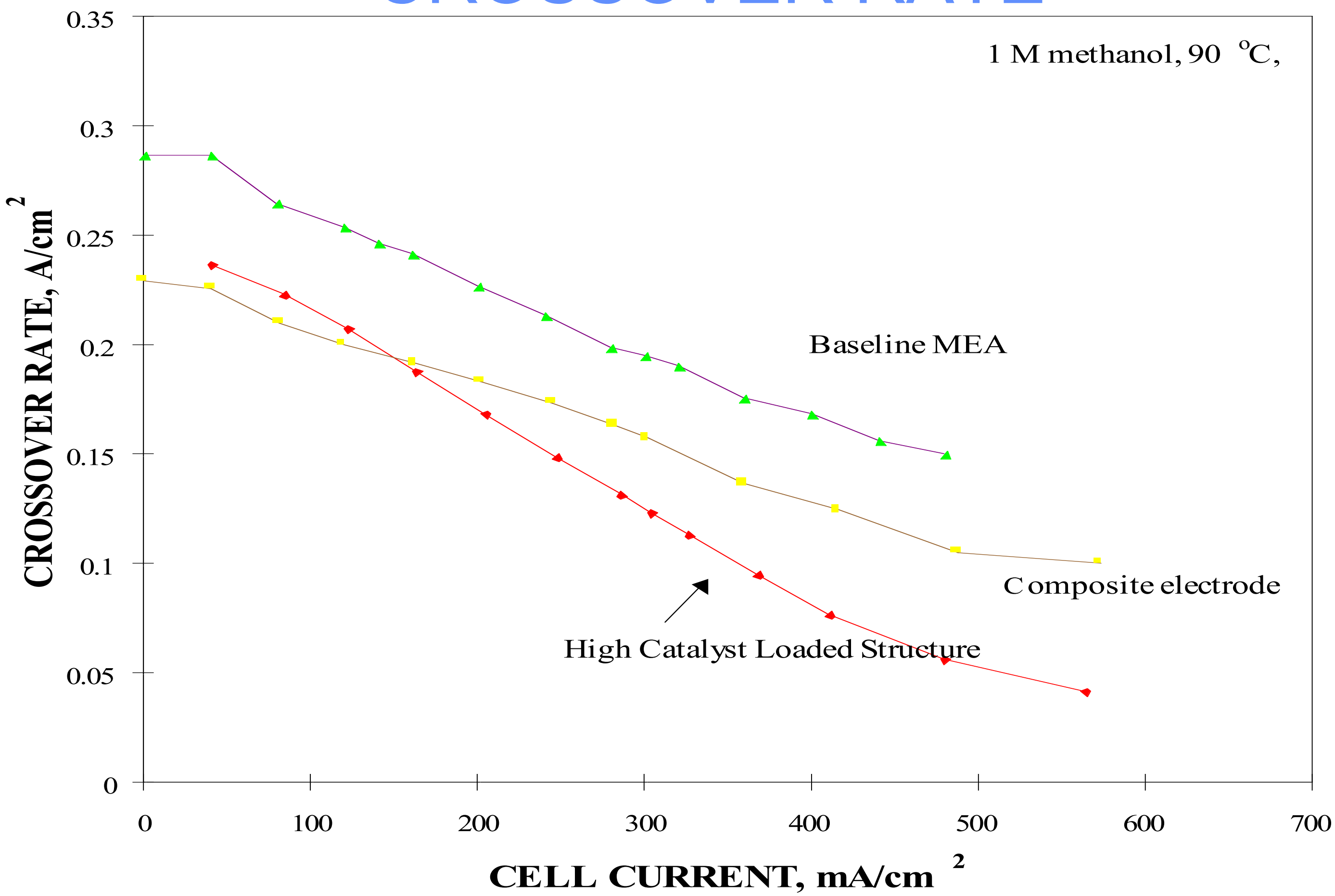
$$k_1/k_2 = \delta_{mem\,1}/\delta_{mem\,2}$$

Experimentally, k_1/k_2= 3.7,
Compares well with 7mil/2mil=3.5

i_{app} = applied current density
i_{cr} = crossover current density
D_{el} = apparent diffusion coefficient in the electrode structure
D_{mem} = apparent diffusion coefficeint in the membrane
A = area
F = Faraday
n = number of electrons/ mole
C^* = concentration of MeOH at the inlet
C = concentration of MeOH adjacent to the edge of membrane

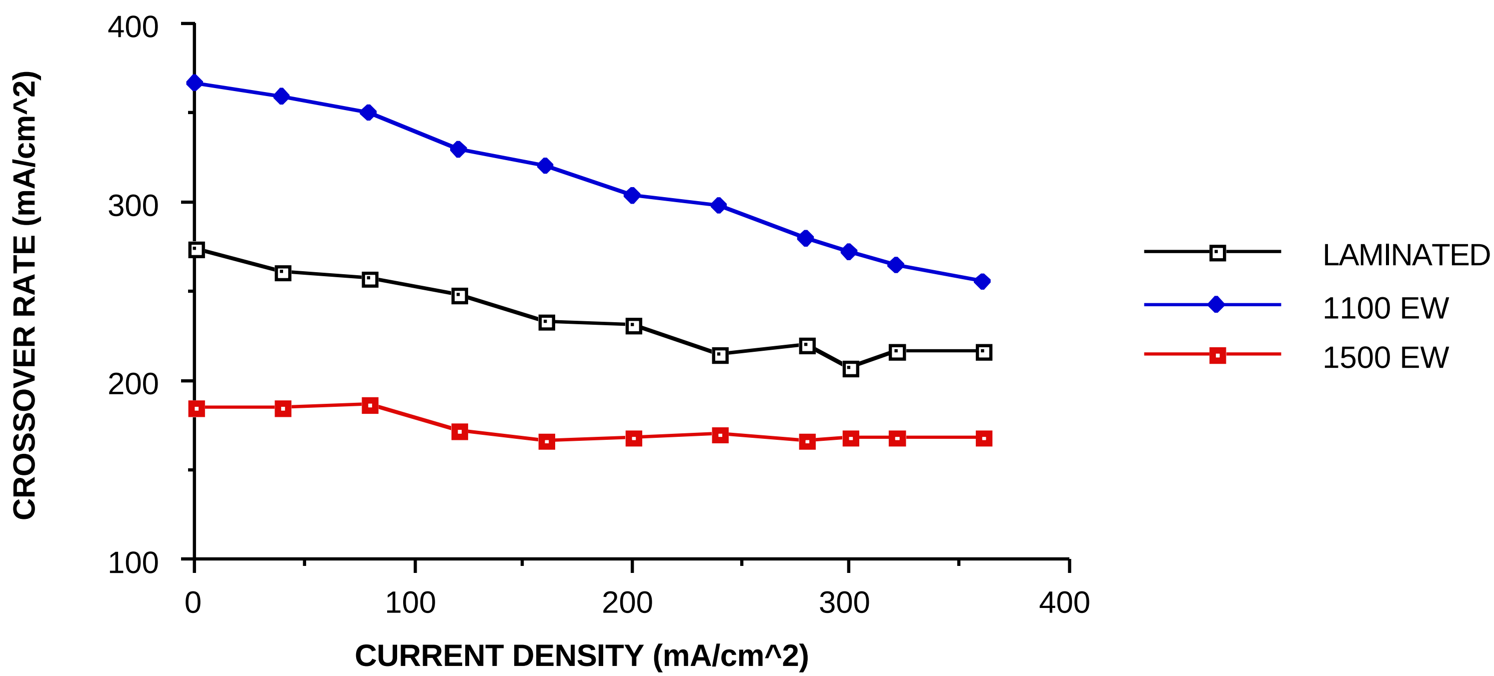


EFFECT OF ELECTRODE STRUCTURE ON CROSSOVER RATE



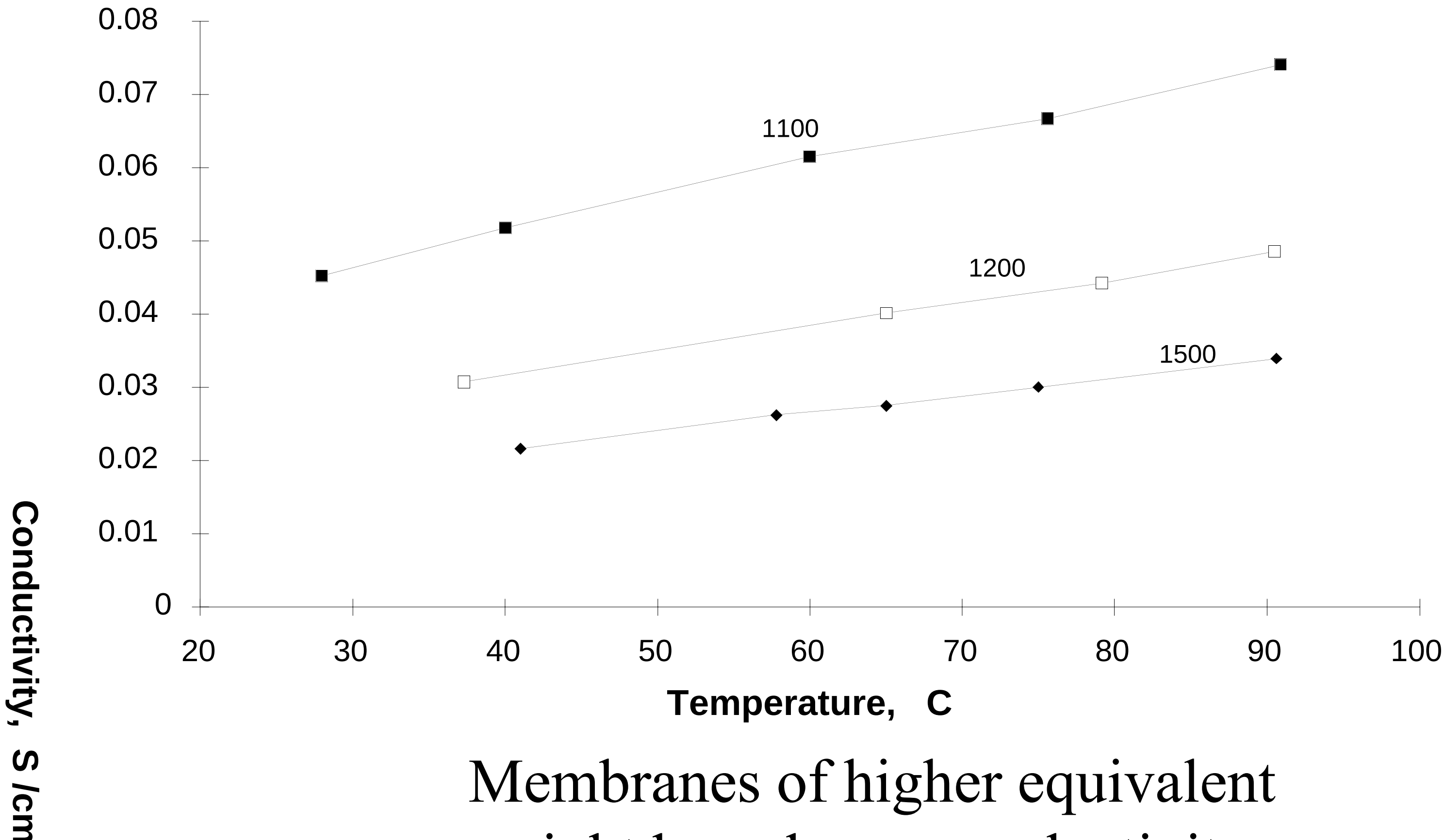
Crossover rate can be modified using different electrode structures

EFFECT OF COMPOSITE LAYERS OF TWO DIFFERENT EQUIVALENT WEIGHTS



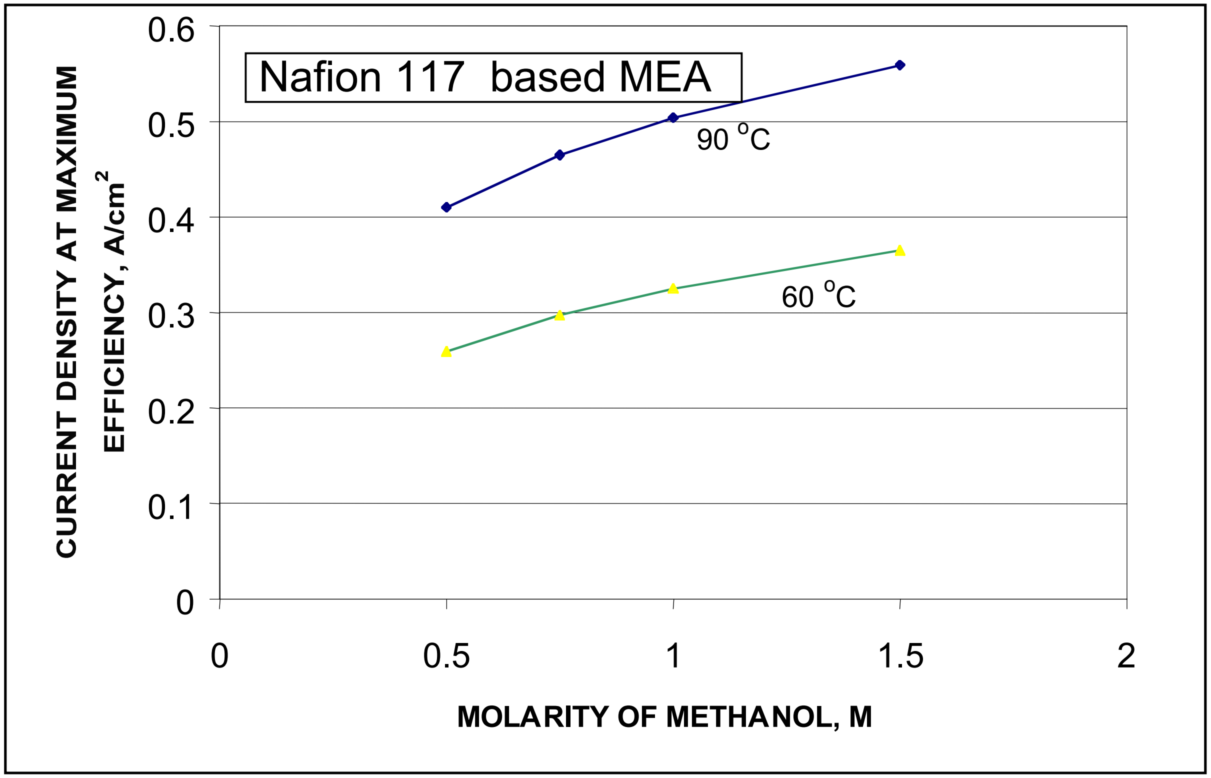
Effect of forming a layer of thin layer of 1500 on 1070 reduces crossover rate

CONDUCTIVITY OF VARIOUS NAFION TYPES



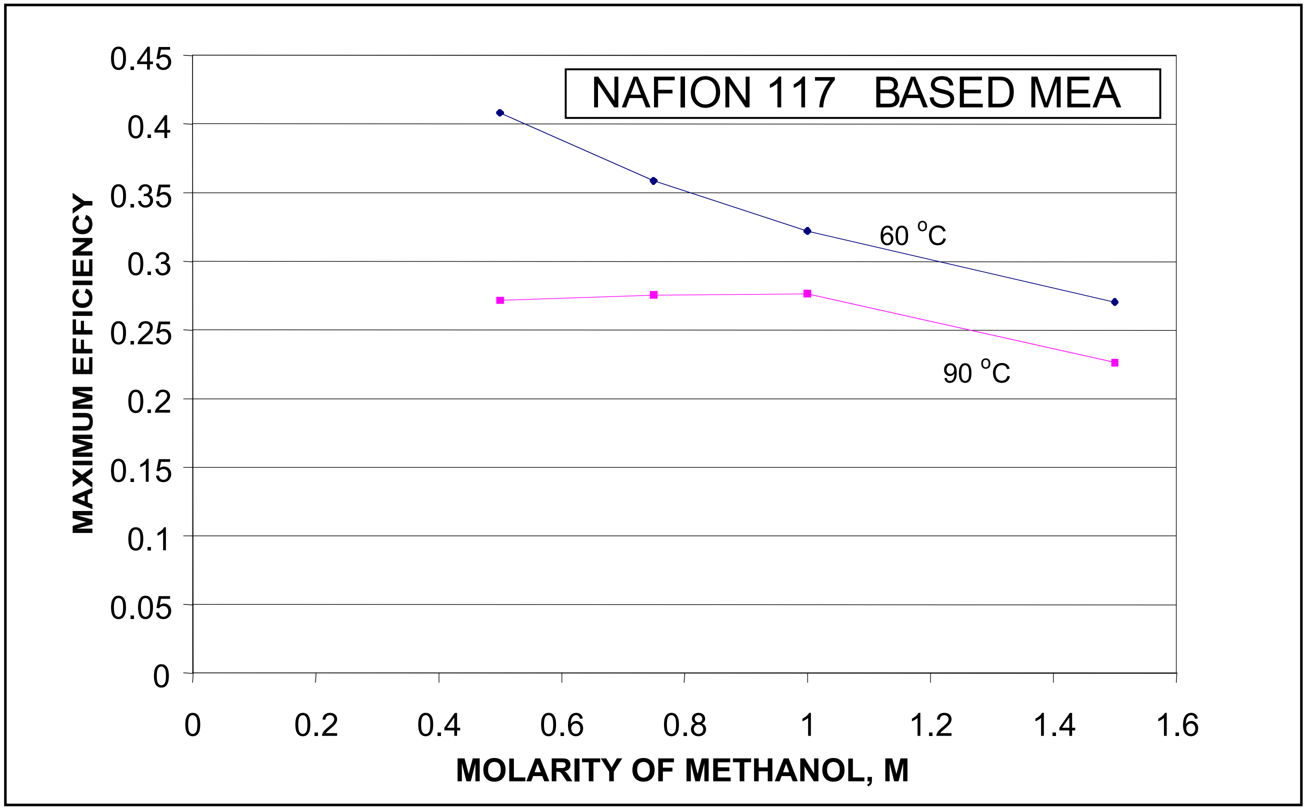
Membranes of higher equivalent weight have lower conductivity

THE CURRENT DENSITY ATTAINED AT MAXIMUM EFFICIENCY



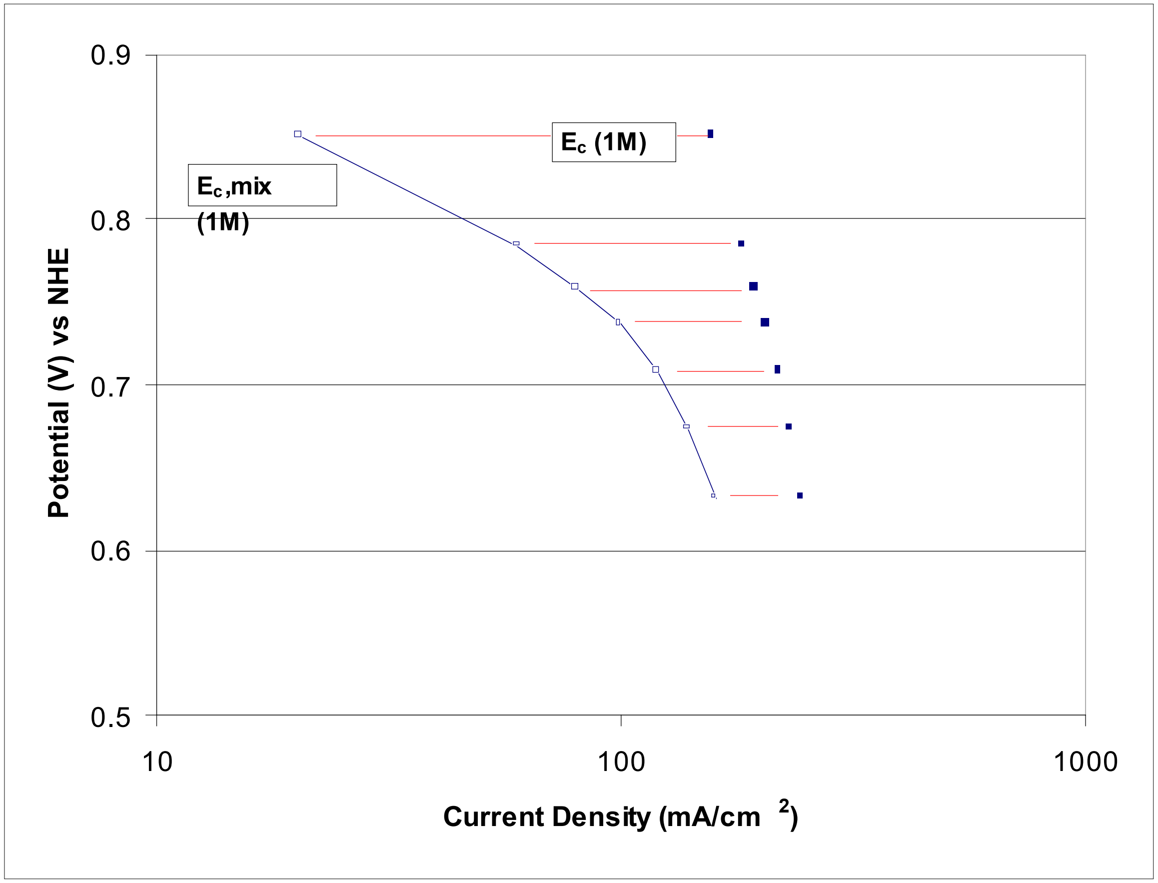
- **Current density at maximum efficiency point increases with temperature and concentration**

EFFECT OF CROSSOVER AND TEMPERATURE ON MAXIMUM EFFICIENCY



- **Maximum efficiency decreases with increasing temperature at all molarities**

CATHODE POTENTIALS, 60°C, 0.1 L/min, AIR

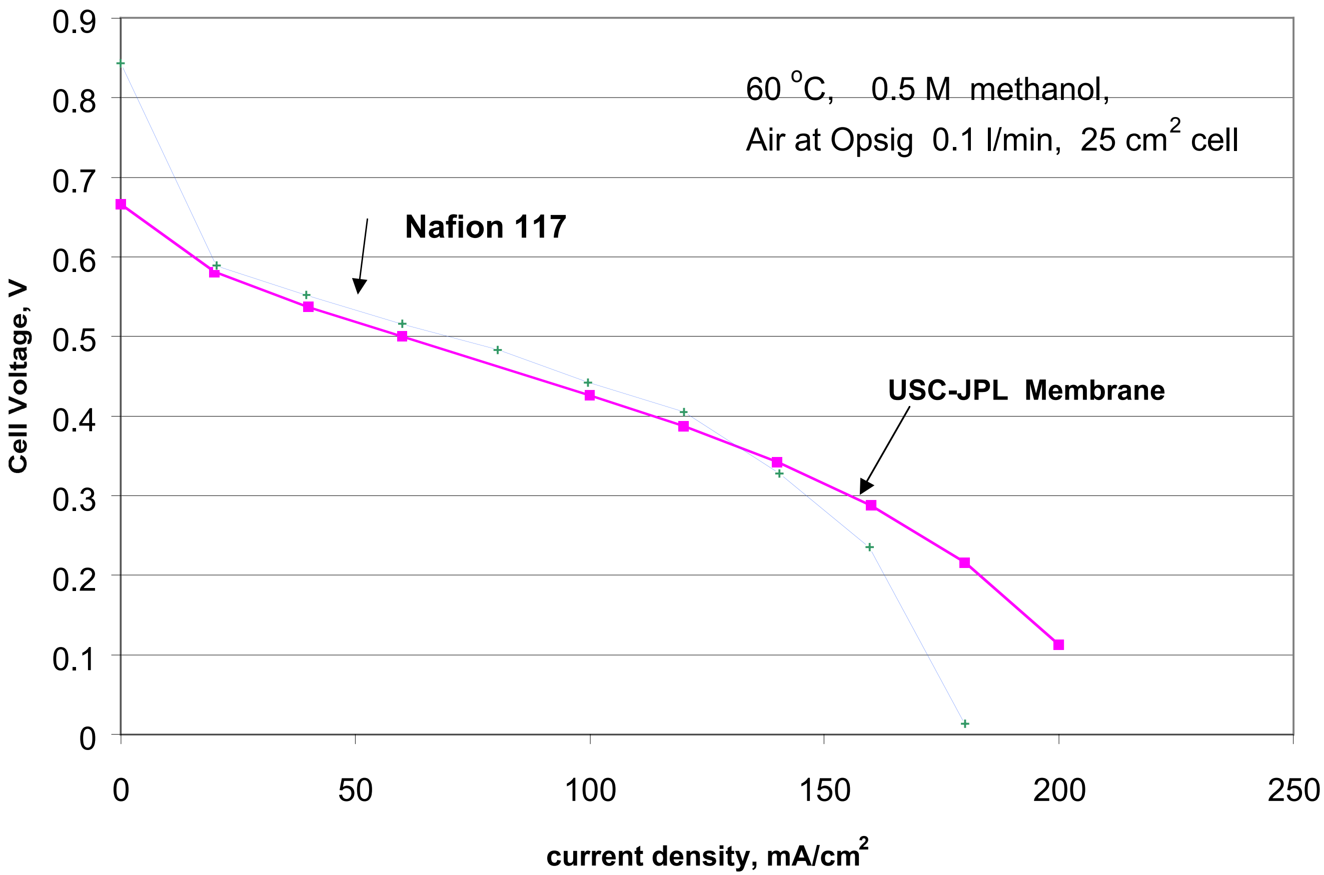


• The DMFC cathode is starved for O_2, when operating on 1M MeOH.

IMPLICATIONS OF NEW MEMBRANE

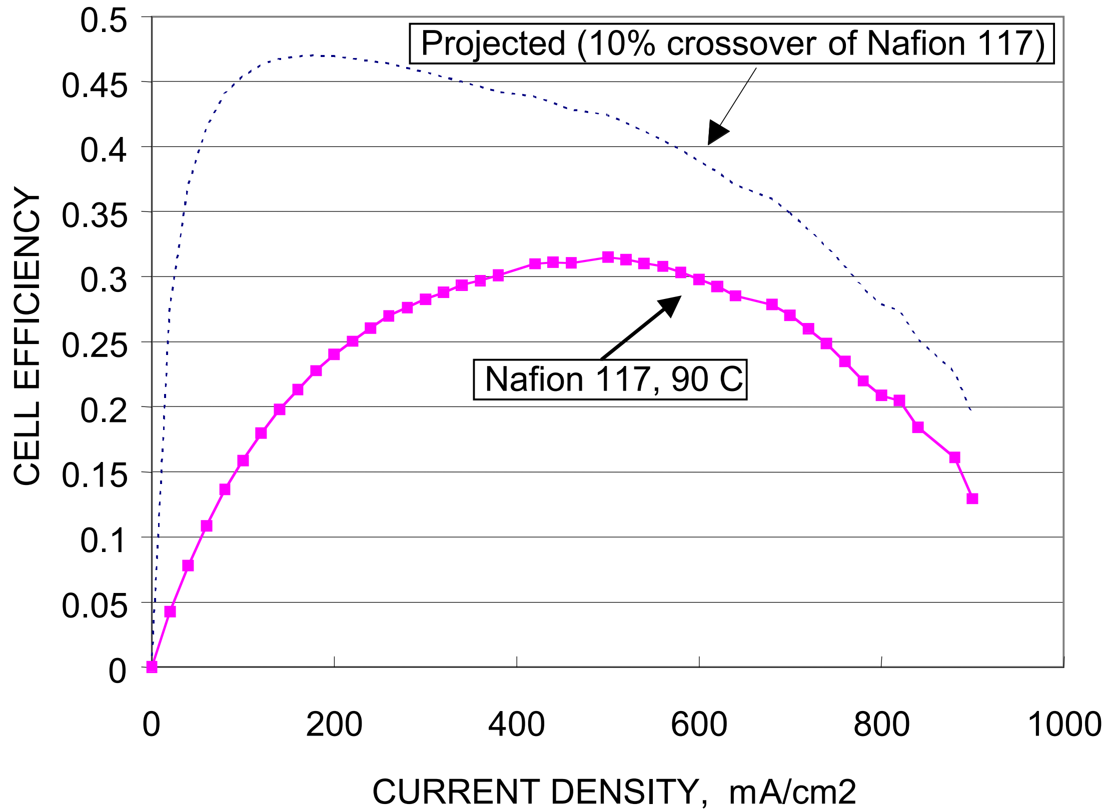
- **Lower water transport**
  - **Allows operation at low air flow rates**
  - **Beneficial for cathode operation**
  - **Dry out possible at higher temperatures**
- **Membrane hydration and conditioning a very slow process**
- **Need to optimize MEA**
  - **Temperature, Pressure, catalyst layer composition etc.**

PERFORMANCE OF LOW CROSSOVER MEMBRANE



Newly developed USC-JPL membranes show
25% of the crossover of Nafion 117 and good performance

PROJECTED IMPROVEMENT IN EFFICIENCY WITH REDUCED CROSSOVER



- **Efficiencies greater than 40% are projected with membranes exhibiting low methanol crossover**

SUMMARY

- **Crossover reduction will allow attainment of higher power densities, by allowing higher concentrations of methanol to be used.**
- **Crossover reduction will reduce air demand**
  - **Higher operating temperature**
  - **Reduced parasitic power loss**
  - **Improved voltage efficiency**
- **Membranes with low permeability will tolerate large variations in methanol concentration**
- **Crossover reduction strategies must not compromise on voltage efficiency**
- **New USC-JPL membrane demonstrated as an example of improved membrane**

ACKNOWLEDGEMENTS

- DARPA AND ARO FOR FUNDING THE WORK
- NASA AND CALTECH FOR FACILITIES